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(54) Process and catalyst for producing poly-ethylene having a broad molecular weight distribution.

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Description

The present invention concerns a process for the polymerization of ethylene. More particularly, the invention relates to processes for the polymerization of ethylene to polyethylene having a broad or multimodal molecular weight distribution.

It is known that certain metallocenes such as bis(cyclopentadienyl) titanium or zirconium dialkyls in combination with aluminum alkyl co-catalyst, form homogeneous catalyst systems useful for the polymerization of ethylene. German Patent Application 2,608,863 discloses the use of a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl)titanium dialkyl, aluminum trialkyl and water. German Patent Application 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula (cyclopentadienyl)$_n$ZrY_{4-n}, wherein n stands for a number in the range of 1 to 4, Y for R, CH_2AlR_2, $CH_2CH_2AlR_2$ and $CH_2CH(AlR_2)_2$ wherein R stands for alkyl or metallo alkyl; an alumiunum trialkyl cocatalyst and water.

European Patent Appln. No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system of (1) a cyclopentadienyl compound of the formula (cyclopentadienyl)$_n$MeY_{4-n} in which n is an integer from 1 to 4, Me is a transition metal, especially zirconium, and Y is either hydrogen, a C_1-C_5 alkyl or metallo alkyl group or a group of the general formula CH_2AlR_2, $CH_2CH_2AlR_2$ and $CH_2CH(AlR_2)_2$ in which R represents a C_1-C_5 alkyl or metallo alkyl group, and (2) an alumoxane.

The above disclosures demonstrate the usefulness of certain specific metallocenes in combination with certain aluminum compounds for the polymerization of ethylene and particularly polymerization at a high activity. The above described catalysts comprising titanium or zirconium metallocenes being homogeneous, produce polyethylenes of narrow molecular weight distribution (MWD) i.e. $\overline{M}w/\overline{M}n$ of from 2-4. Hence, the references neither disclose polyethylenes having a broad molecular weight distribution and/or a multimodal molecular weight distribution, nor how to obtain such polyethylenes.

U. S. Patent 4,310,648 discloses a catalytic reaction product of a titanium compound, a zirconium compound, an organomagnesium compound and a halide source. The reaction product (a heterogeneous catalyst) when employed in combination with aluminum alkyls is useful for the production at high activity of broad molecular weight polyethylenes.

U. S. Patent 4,361,685 discloses the use of organic soluble chrominum and zirconium compounds to be employed in combination with a supported catalyst system comprising an organometallic activating agent and a trivalent or tetravalent titanium compound. The polymers obtained have a high molecular weight and a narrow molecular weight distribution.

In " Molecular Weight Distribution And Stereoregularity Of Polypropylenes Obtained With $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3$ Catalyst System"; Polymer, Pg. 469-471, 1981, Vol. 22, April, Doi, et al disclose propylene polymerization with a catalyst which at about 41°Cobtains a soluble catalyst and insoluble catalyst fraction, one with "homogeneous catalytic centres" and the other with "heterogeneous catalytic centres". The polymerization at that temperature obtains polypropylene having a bimodal molecular weight distribution.

It is highly desirable to have for many application, such as an extrusion and molding processes, polyethylenes which have a broad molecular weight distribution of the unimodal and/or the multimodal type. Such polyethylenes evidence excellent processability, i.e., they can be processed at a faster throughput rate with lower energy requirements and at the same time such polymers would evidence reduced melt flow perturbations.

In view of the foregoing problems, it would be highly desirable to provide a polymerization process of high activity to produce high quality ethylene polymers which evidence broad molecular weight distribution. It is furthermore highly desirable to be able to produce the ethylene polymers directly by a process requiring a single reactor, i.e. without having to blend polyethylenes having different molecular weights and distributions in order to obtain the advantages of this invention.

SUMMARY OF THE INVENTION

Accordingly there is provided a process for producing polyethylene which comprises polymerising ethylene in the presence of a catalyst system comprising (a) a common alumoxan as a cocatalyst component and (b1) a catalytic amount of a first metallocene having first propagation and termination rat constants suitable for providing, with such alumoxan , a polymer having a narrow MWD with an Mw at a first value; and (b2) a catalytic amount of a second metalloc ne having s cond propagation and termination rate constants different from the first suitable for providing, with such alumoxane a polymer having a narrow MWD with an Mw at a s cond value different from th first value, said metallocenes being mono, di or

tricyclopentadienyl derivatives of a Group 4b, 5b or 6b transition metal and the respective different metallocenes being used as transition m tal catalyst component in proportions selected such as to provide a desired broad or multimodal MWD in conjunction with one another. The metallocenes employed in accordance with this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of a transition metal of Group 4b, 5b and 6b metals of the Periodic Table and include mono, di and tricyclopentadienyls and their derivatives of the transition metals. The metallocenes can be represented by the general formula $(C_5R'_m)_pR''_s(C_5R'_m)MeQ_{3-p}$ or $R''_s(C_5R'_m)_2MeQ'$ wherein $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R', which can be the same or different, is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms of the cyclopentadienyl ring are joined together to form a C_4-C_6 ring, R" is a C_1-C_4 alkylene radical, a dialkyl germanium or silicone or an alkyl phosphine or amine radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbon radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to 20 carbon atoms, Me is a Group 4b, 5b and 6b metal of the Periodic Table (Chemical Rubber Company's Handbook of Chemistry and Physics, 48th Edition), s is 0 or 1, p is 0, 1 or 2; when p = 0, s = 0; m is 4 when s is 1 and m is 5 when s is 0.

The present invention especially provides a process for producing polyethylenes having a high molecular weight as well as a multimodal molecular weight distribution and especially MWD of the bimodal type. In the process ethylene may be polymerised alone or with minor amounts of higher alpha-olefins. The Mw/Mn ratio may be between 2 to 50. In accordance with this invention one can advantageously tailor polyethylene having desired molecular weights and molecular weight distributions by the judicious selection of metallocenes.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a plot of the molecular weight distribution of polyethylene prepared as in Example 1 and in accordance with this invention.

Figure 2 is a plot of the molecular weight distribution of polyethylene prepared as in comparative example 1B showing a narrow unimodal MWD.

Figure 3 is a plot of the molecular weight distribution of polyethylene prepared as in comparative example 1A showing a narrow unimodal MWD.

Figure 4 is a plot of the molecular weight distribution of polyethylene prepared as in example 2 and showing a bimodal MWD.

Figure 5 is a plot of the molecular weight distribution of polyethylene prepared as in example 3 showing a bimodal MWD.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed towards a process for the catalytic polymerization of ethylene to high molecular weight polyethylenes evidencing a broad and/or multimodal molecular weight distribution. The polymers are intended for fabrication into articles by extrusion, injection molding, thermoforming or rotational molding. In particular, the polymers of this invention are homopolymers of ethylene, however, minor amounts of higher alpha-olefins having from 3 to 10 carbon atoms and preferably 4 to 8 carbon atoms can be copolymerized with ethylene. Illustrative of the higher alpha-olefins are butene-1, hexene-1 and octene-1.

In the process of the present invention, ethylene, either alone or together with minor amounts of alpha-olefins, is polymerized in the presence of a catalyst system comprising at least two metallocenes and an alumoxane.

The alumoxanes are well known in the art and are polymeric aluminum compounds which can be represented by the general formulae $(R\text{-}Al\text{-}O)_n$ which is a cyclic compound and $R(R\text{-}Al\text{-}O\text{-})_nAlR_2$, which is a linear compound. In the general formula R is a C_1-C_5 alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 1 to 20. Most preferably, R is methyl. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds ar obtained.

The alumoxanes can be prepared in various ways. Preferably, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as benzen or an aliphatic hydrocarbon. For example, the aluminum alkyl is treat d with wat r in the form of a moist solvent or the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a

hydrated salt such as hydrated copper sulfate.

Preferably, the alumoxane is prepared in the presence of a hydrated copper sulfate. The method comprises tr ating a dilut solution of aluminum trimethyl in, for example, toluene, with copper sulfate represented by the general formula $CuSO_4.5H_2O$. The ratio of copper sulfate to aluminum trimethyl is desirably about 1 mole of copper sulfate for 5 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

The metallocenes employed each should have different propagation and termination rate constants with respect to ethylene polymerization. Such rate constants can be determined by one of ordinary skill in the art. The metallocenes are the organometallic coordination compound which are the mono, di and tricyclopentadienyls and their derivatives of a transition metal of Group 4b, 5b and 6b metals of the Periodic Table. The more desirable metallocenes employed in accordance with the invention are represented by the general formula $(C_5R'_m)_pR''_s(C_5R'_m)MeQ_{3-p}$ and $R''s(C_5R'_m)_2MeQ'$ wherein $(C_5R'_m)$ is cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals containing from 1 to 20 carbon atoms or two adjacent carbon atoms are joined together to form a C_4-C_6 ring, R" is a C_1-C_4 alkylene radical, a dialkyl (germanium or silicon) or an alkyl (phosphine or amine) radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1-20 carbon atoms or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 or 1, p is 0, 1 or 2; when p is 0, s is 0; m is 4 when s is 1 and m is 5 when s is 0 and Me is a Group 4b, 5b or 6b metal of the Periodic Table.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl and phenyl.

Exemplary alkylene radicals are methylene, ethylene and propylene.

Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred.

Exemplary of the alkylidene radicals is methylidene, ethylidene and propylidene.

The multiple metallocene system usefully employed in accordance with this invention are preferably the mono, bi and tricyclopentadienyl or substituted cyclopentadienyl titanium (IV) and zirconium (IV) compounds represented by the general formula.

Illustrative but non-limiting examples of the titanocenes which can be usefully employed in accordance with this invention are monocyclopentadienyl titanocenes, such as cyclopentadienyl titanium trichloride, pentamethylcyclopentadienyl titanium trichloride; bis(cyclopentadienyl) titanium diphenyl, the carbene represented by the formula $Cp_2Ti=CH_2 \cdot Al(CH_3)_2Cl$, and derivatives of this reagent such as

$$Cp_2Ti=CH_2 \cdot Al(CH_3)_3,\ (Cp_2TiCH_2)_2,$$
$$Cp_2\underline{TiCH_2CH(CH_3)CH_2},\ Cp_2\underline{Ti=CHCH_2CH_2},$$
$$Cp_2Ti=CH_2 \cdot AlR'''_2Cl,$$

wherein Cp is a cyclopentadienyl or substituted cylopentadienyl radical, and R''' is an alkyl, aryl or alkylaryl radical having from 1-18 carbon atoms; substituted bis(Cp)Ti(IV) compounds such as bis(indenyl)Ti diphenyl or dichloride, bis(methylcyclopentadienyl)Ti diphenyl or dihalides and other dihalide complexes; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds, such as bis(1,2-dimethylcyclopentadienyl)Ti diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)Ti diphenyl or dichloride and other dihalide complexes.

Illustrative but non-limiting examples of the zirconocenes which can be usefully employed in accordance with this invention are monocyclopentadienyl zirconocenes, such as cyclopentadienyl zirconium trichloride, pentamethyl cyclopentadienyl zirconium trichloride; bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, the alkyl substituted cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium dimethyl, bis(β-phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, and dihalide complexes of the above. Di-alkyl, tri-alkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis (1,2-dimethylcyclopentadienyl)zirconium dimethyl, bis(1,3-diethylcyclopentadienyl)zirconium dimethyl and dihalide complexes of the abov . Silicon, phosphorus, and carbon bridg d cyclop ntadiene complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide, methylphosphine dicyclopentadienyl zirconium dimethyl or dihalid , and methylene dicyclopentadienyl zirconium dimethyl or dihalide, carbenes represented by the formulae $Cp_2Zr=CH_2P(C_6H_5)_2CH_3$, and derivatives of these compounds such as

$$Cp_2ZrCH_2CH(CH_3)CH_2.$$

Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)-vanadium dichloride are illustrative of other metallocenes.

The ratio of aluminum in the alumoxane to total metal in the metallocenes can be in the range of 0.5:1 to 10^5:1, and preferably 5:1 to 10^3:1. The molar ratio of zirconocene to titanocene can vary over a wide range and in accordance with this invention the only limitation on the molar ratios is the breadth of the MW distribution or the degree of bimodality desired in the product polymer. Desirably, the zirconocene to titanocene molar ratio will be 1:100 to 100:1, and preferably 1:10 to 1:1.

The solvents used in the preparation of the catalyst system are inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents are well known and include, for example, butane, isobutane, pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene or xylene.

The catalyst systems described herein are suitable for the polymerization of ethylene either in solution, slurry or gas phase over a wide range of temperatures and pressures. For example, such temperatures may be in the range of -60°C to 280°C and especially in the range of 50°C to 160°C. The pressures employed in the process of the present invention are those well known for, for example, in the range of 1 to 500 atmospheres and even greater.

In a solution phase polymerization the alumoxane and metallocene can be employed as a homogeneous catalyst system. The alumoxane is preferably dissolved in a suitable solvent, typically in inert hydrocarbon solvent such as toluene or xylene, in molar concentrations of 0.1M to 3M, however, greater or lesser amounts can be employed.

The soluble metallocenes can be converted to supported heterogeneous catalyst by depositing said metallocenes on typical catalyst supports such as, for example, silica, alumina, and polyethylene. The solid catalysts in combination with an alumoxane can be usefully employed in slurry and gas phase olefin polymerization.

After polymerization and deactivation of the catalyst, the product polymer can be recovered by processes well known in the art for removal of deactivated catalysts and solution. The solvents may be flashed off from the polymer solution and the obtained polymer extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives, as is known in the art, may be added to the polymer.

The polymer product obtained from the process in accordance with this invention will have an average molecular weight in the range of 500 to 2,000,000 and preferably 10,000 to 500,000. The polymer will also have concentrations of average molecular weights in the range of 500 to 100,000 and 100,000 to 1,000,000 for each sample.

The polymers produced by the process of this present invention are capable of being fabricated into a wide variety of articles, as is known for homopolymers of ethylene and copolymers of ethylene and higher alpha-olefins. The present invention is illustrated by the following examples.

In the examples following the molecular weights were determined on a Water's Associates Model No. 150C GPC (Gel Permeation Chromatography). The measurements were made by dissolving polymer samples in hot trichlorobenzene (TCB) and filtered. The GPC runs were performed at 145°C in TCB at 1.5 ml/min using two Shodex A80 M/S Gel columns of 9.4 mm internal diameter from Perkin Elmer Inc. 300 milliliter of 3.1 percent solutions in TCB were injected and the chromotagraphic runs monitored at sensitivity equal -64 and scale factor equal 65. The samples were run in duplicate. The integration parameters were obtained with a Water's Associates data module. An antioxidant, N-phenyl-2-naphthylamine, was added to all samples.

EXAMPLES

In the examples following the alumoxane was prepared in the following manner:

600cc of a 14.5% solution of trim thylaluminum (TMA) in heptane was added in 30cc increments at 5 minute intervals, with rapid stirring, to 200cc toluene in a Zippoclave reactor und r nitrogen and maintained at 100°C. Each increment was imm diately followed by the addition of 0.3cc water. Th reactor was vented of methane after each addition. Upon completion of the addition, the reactor was stirred for 6 hours while maintaining the temperatur at 100°C. Th mixtur , contains soluble alumoxane and insolubl materials, is allowed to cool to room temperatur and settle. The clear solution containing the soluble alumoxane is

separated by decantation from the solids.

Example 1

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 500cc of dry, degassed toluene was introduced directly into the pressure vessel. 20.0cc of alumoxane solution (0.64 molar in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0 psig of nitrogen. 0.091 mg bis(pentamethyl cyclopentadienyl)zirconium dimethyl dissolved in 1.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel followed by the injection of 0.906 mg bis(cyclopentadienyl) titanium diphenyl in 10 ml of toluene. After 1 minute, ethylene at 50 psig was admitted and while the reaction vessel was maintained at 50°C. The ethylene was passed into the vessel for 40 minutes at which time the reaction was stopped by rapidly venting and cooling the reactor. 20.1 gms of powdery white polyethylene having a $\overline{M}n$ of 58,600 and a $\overline{M}w$ of 323,000 with a molecular weight distribution of 5.51. The GPC as shown in Fig. 1 showed a bimodal molecular weight distribution.

Comparative Example 1A

Ethylene was polymerized under conditions identical to that of Example 1 with the exception that the zirconocene only was employed in combination with the alumoxane. 0.102 mg of the zirconocene was employed. 20.6 gm of polyethylene was obtained. The polyethylene had a $\overline{M}n$ of 42,000 and $\overline{M}w$ of 139,000 with a MWD of 3.31. The GPC as appears in Figure 3 evidenced a unimodal molecular weight distribution.

Comparative Example 1B

Ethylene was polymerized under conditions identical to that of Example 1 with the exception that the titanocene only was employed in combination with the alumoxane. 1.02 mg of the titanocene was employed. 13.2gm of polyethylene was obtained. The polyethylene had a $\overline{M}n$ of 184,000 and $\overline{M}w$ of 558,000 with a MWD of 3.03. The GPC as appears in Figure 2 evidenced a unimodal molecular weight distribution.

Example 2

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 20.0cc of alumoxane (8 mmoles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of nitrogen. 0.015 mg bis(cyclopentadienyl) zirconium dimethyl dissolved in 1.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel followed by the injection of 5.18 mg bis(cyclopentadienyl)titanium diphenyl in 10 ml of toluene. After 1 minute, ethylene at 60 psig was admitted for 40 minutes while maintaining the reaction vessel at 80°C. The reaction was stopped by rapidly venting and cooling. 10.7 gms of powdery white polyethylene having a $\overline{M}n$ of 63,000 and a $\overline{M}w$ of 490,000 with a molecular weight distribution of 7.8. The GPC as shown in Fig. 4 showed a bimodal molecular weight distribution.

Example 3

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrog n flow. 400cc of dry, degassed toluene was introduced dir ctly into the pressure vessel. 20.0cc of alumoxane (8 mmoles in total aluminum) was injected into the v ssel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0 psig of nitrogen. 0.151 mg bis(cyclop ntadi nyl) zirconium dim thyl dissolv d in 1.0 ml of dry, distilled toluen was inj cted through th septum inl t into th v ssel follow d by the injection of 5.5 mg bis(cyclopentadienyl) titanium diph nyl in 10 ml of toluene. After 1 minute, ethylen at 60 psig was admitted

for 40 minutes while maintaining the reaction vessel at 50°C. The reaction was stopped by rapidly v nting and cooling. 13.8 gms of powdery white polyethylene having a $\overline{M}n$ of 16,500 and a $\overline{M}w$ of 89,000 with a mol cular weight distribution of 5.4. The GPC as shown in Fig. 5 showed a bimodal molecular w ight distribution.

Example 4

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 20.0cc of alumoxane (15 mmoles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of nitrogen. 0.231 mg bis(cyclopentadienyl) zirconium dimethyl and 0.260 bis-(ethylcyclopentadienyl)zirconium dimethyl, each dissolved in 1.0 ml of dry distilled toluene, were injected through the septum inlet into the vessel followed by the injection of 0.535 mg bis(cyclopentadienyl)titanium diphenyl in 10 ml of toluene. After 1 minute, ethylene at 60 psig was admitted for 40 minutes while maintaining the reaction vessel at 80°C. The reaction was stopped by rapidly venting and cooling. 24.0 gms of powdery white polyethylene having a $\overline{M}n$ of 43,000 and a $\overline{M}w$ of 191,000 with a molecular weight distribution of 4.4.

Example 5

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 20.0cc of alumoxane (15 mmoles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of nitrogen. .201 mg bis(cyclopentadienyl)zirconium dimethyl and 0.216 mg bis(ethyl cyclopentadienyl)zirconium dimethyl each dissolved in 1.0 ml of dry distilled toluene were injected through the septum inlet into the vessel followed by the injection of 0.506 mg bis(cyclopentadienyl) titanium diphenyl in 10 ml of toluene. After 1 minute, ethylene at 50 psig was admitted for 40 minutes while maintaining the reaction vessel at 80°C. The reaction was stopped by rapidly venting and cooling. 25.2 gms of powdery white polyethylene having a $\overline{M}n$ of 39,700 and a $\overline{M}w$ of 168,000 with a molecular weight distribution of 4.2 and bimodal $\overline{M}w$ distribution.

Example 6

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 500cc of dry, degassed toluene was introduced directly into the pressure vessel. 10.0cc of alumoxane (8 moles total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of nitrogen. 0.260 mg bis(cyclopentadienyl)zirconium dimethyl and 0.204 mg bis(ethyl cyclopentadienyl)zirconium dimethyl each dissolved in 1.0 ml of dry distilled toluene were injected through the septum inlet into the vessel. After 1 minute, ethylene at 60 psig was admitted for 12 minutes while maintaining the reaction vessel at 80°C. The reaction was stopped by rapidly venting and cooling. 32.0 gms of powdery white polyethylene having a $\overline{M}n$ of 47,100 and a $\overline{M}w$ of 183,000 with a molecular weight distribution of 3.9.

Claims

1. A process for producing polyethylene which comprises polymerising ethylene in the presence of a catalyst system comprising (a) a common alumoxan as a cocatalyst compon nt and (b1) a catalytic amount of a first metalloc ne having first propagation and termination rat constants suitabl for providing, with such alumoxane, a polymer having a narrow MWD with an Mw at a first value; and (b2) a catalytic amount of a s cond metallocen having s cond propagation and termination rate constants different from the first and suitabl for providing, with such alumoxan a polym r having a narrow, MWD with an Mw at a s cond value diff r nt from th first valu , said m tallocenes b ing mono, di or

tricyclopentadienyl derivatives of a Group 4b, 5b or 6b transition m tal and the respective different metalloc nes being used as transition m tal catalyst component in proportions selected such as to provide a desired broad or multimodal MWD in conjunction with one another.

2. A process according to claim 1 in which at least one of the metallocenes is a zirconocene.

3. A process according to claim 2 in which two different zirconocenes are used.

4. A process according to claim 1 in which two different titanocenes are used.

5. A process according to claim 3 in which at least two different zirconocenes and one titanocene are used.

6. A process according to claim 4 in which at least two different titanocenes and one zirconocene are used.

Revendications

1. Procédé de production de polyéthylène, qui consiste à polymériser de l'éthylène en présence d'une composition de catalyseur comprenant (a) un alumoxane usuel comme constituant servant de co-catalyseur, et (b1) une quantité catalytique d'un premier métallocène ayant des premières constantes de vitesse de propagation et de terminaison convenant pour la production, avec un tel alumoxane, d'un polymère ayant une DPM étroite, avec une Mp égale à une première valeur ; et (b2) une quantité catalytique d'un second métallocène ayant des secondes constantes de vitesse de propagation et de terminaison différentes des premières et convenant pour la production, avec un tel alumoxane, d'un polymère ayant une DPM étroite, avec une Mp égale à une seconde valeur différente de la première valeur, lesdits métallocènes étant des dérivés de mono-, di- ou tricyclopentadiényle d'un métal de transition du Groupe 4b, 5b ou 6b et les métallocènes différents respectifs étant utilisés en association les uns avec les autres comme constituant de catalyseur renfermant un métal de transition en des proportions choisies de manière à parvenir une DPM large ou multimodale désirée.

2. Procédé suivant la revendication 1, dans lequel au moins l'un des métallocènes est un zirconocène.

3. Procédé suivant la revendication 2, dans lequel deux zirconocènes différents sont utilisés.

4. Procédé suivant la revendication 1, dans lequel deux titanocènes différents sont utilisés.

5. Procédé suivant la revendication 3, dans lequel au moins deux zirconocènes différents et un titanocène sont utilisés.

6. Procédé suivant la revendication 4, dans lequel au moins deux titanocènes différents et un zirconocène sont utilisés.

Patentansprüche

1. Verfahren zur Herstellung von Polyethylen, bei dem man Ethylen in Gegenwart eines Katalysatorsystems polymerisiert, das (a) ein gebräuchliches Alumoxan als eine Cokatalysatorkomponente, (b1) eine katalytische Menge eines ersten Metallocens mit ersten Propagations- und Abbruchgeschwindigkeitskonstanten, das geeignet ist, mit dem Alumoxan ein Polymer mit einer engen Molekulargewichtsverteilung mit einem Mw bei einem ersten Wert zu ergeben, und (b2) eine katalytische Menge eines zweiten Metallocens mit zweiten, von den ersten verschiedenen Propagations- und Abbruchgeschwindigkeitskonstanten, das geeignet ist, mit dem Alumoxan ein Polymer mit einer engen Molekulargewichtsverteilung mit einem Mw bei einem zw it n, von dem rsten Wert verschiedenen Wert zu ergeben, umfaßt, wobei die Metalloc ne Mono-, Di- oder Tricyclopentadienylderivat eines Grupp 4b, 5b oder 6b Übergangsmetalls sind und di jeweiligen verschiedenen Metallocene als Übergangsmetallkatalysatorkompon nten in Anteilen v rwend t werden, di so gewählt sind, daß si in V rbindung mit inander eine gewünschte breit oder multimodale Molekulargewichtsv rteilung liefern.

2. Verfahren nach Anspruch 1, bei d m mind stens eines der M tallocene ein Zirkonoc n ist.

3. Verfahren nach Anspruch 2, bei dem zwei verschiedenen Zirkonoc ne verwendet werden.

4. Verfahren nach Anspruch 1, bei dem zwei verschiedene Titanocene verwendet werden.

5. Verfahren nach Anspruch 3, bei dem mindestens zwei verschiedene Zirkonocene und ein Titanocen verwendet werden.

6. Verfahren nach Anspruch 4, bei dem mindestens zwei verschiedene Titanocene und ein Zirkonocen verwendet werden.

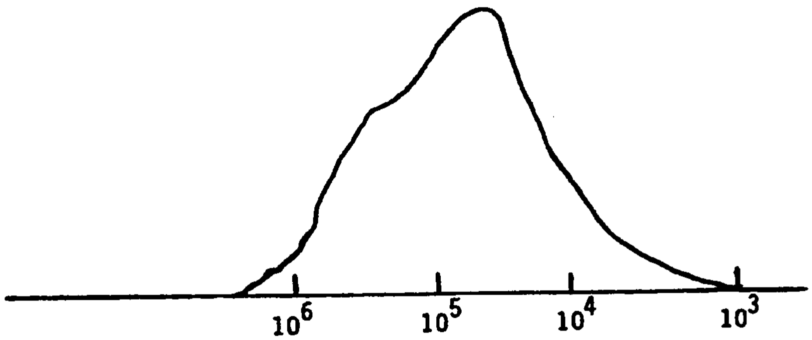

FIG. 1

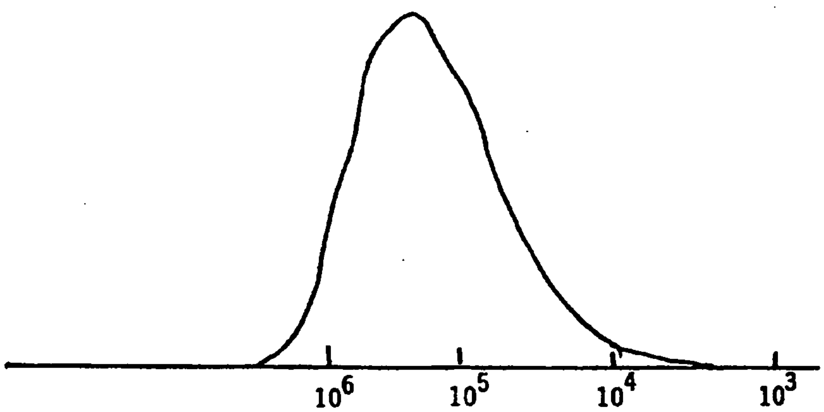

FIG. 2

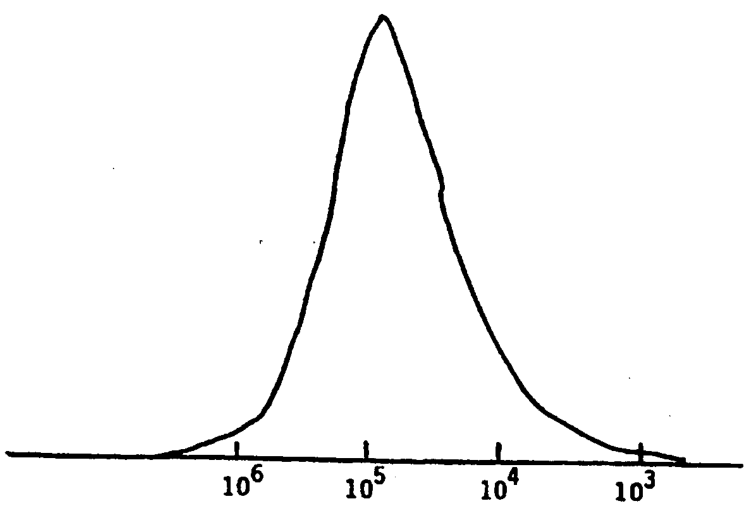

FIG. 3

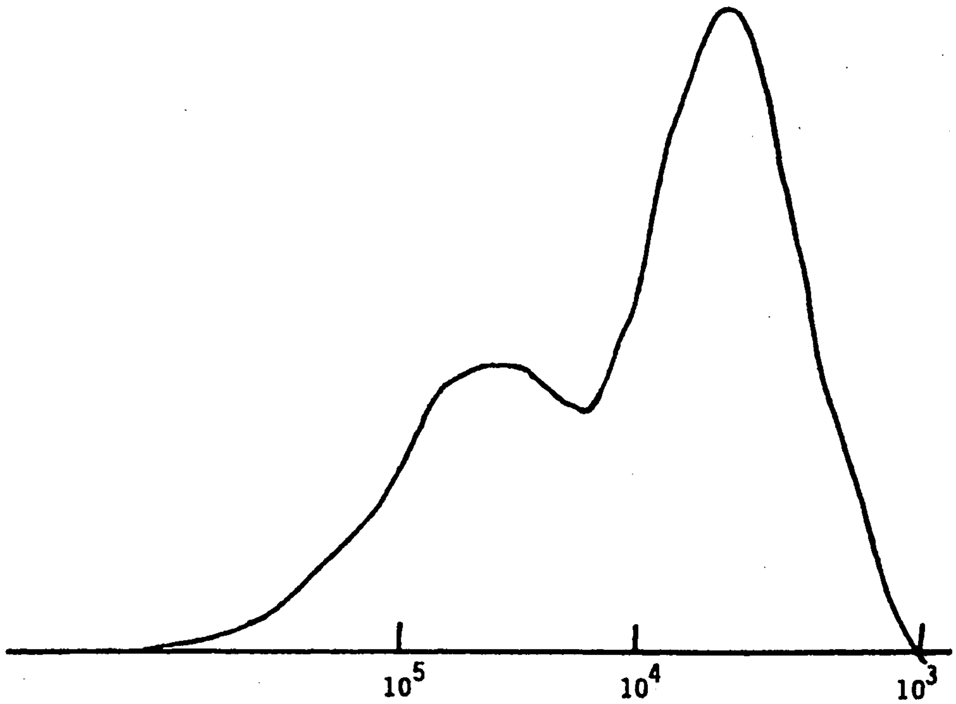

FIG. 4

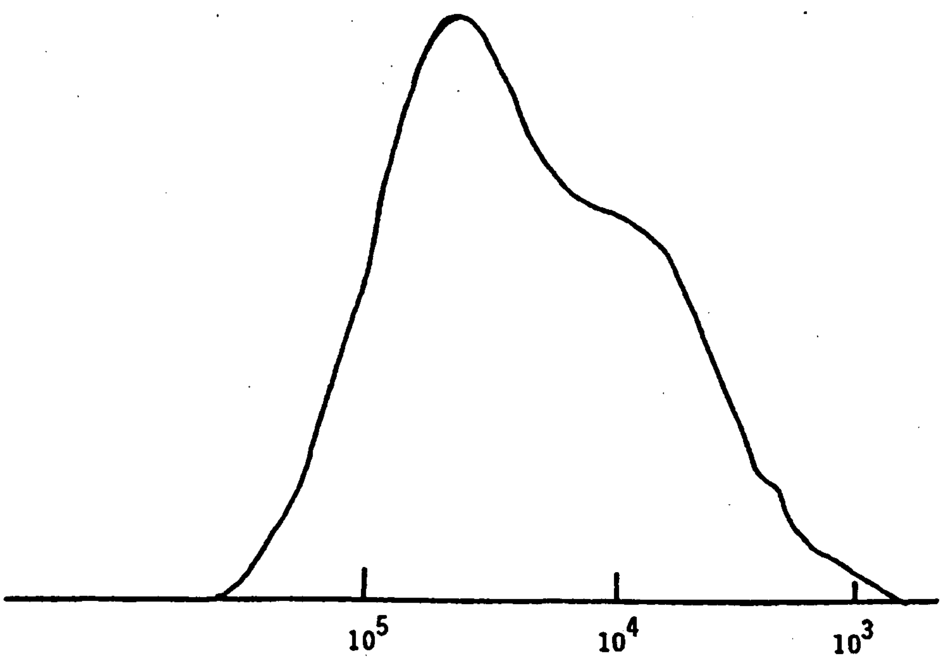

FIG. 5